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The Effect of Surfactant on Flow of Spontaneously Condensing Steam in Laval Nozzles

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Abstract—Different mechanisms of the possible effect of surfactant on the condensation of supercooled steam in transonic nozzles are considered.

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Surfactants find extensive application in various branches of industry owing to a number of special features, the most important of which include adsorption on the interfaces and the capability of reducing the surface tension. One of the most advanced surfactants is octadecylamine (ODA) $C_{18}H_{37}NH_2$, which falls under the category of higher aliphatic amines.

Experimental investigations [1] revealed a significant effect of ODA additions on the process of nonequilibrium spontaneous condensation of supercooled steam in Laval nozzles. This effect shows up in the faster emergence of the condensed phase, in the shift of condensation jump downstream, in the growing average size of droplets formed, in the degeneracy of condensation jump in the case of high concentrations of surfactant, in the stabilization of unsteady flow, and in the transition from self-oscillatory to steady quasi-equilibrium flow. It was demonstrated in [1, 2] that these experimental results are in qualitative agreement with the results of calculations performed using the model of homogeneous (spontaneous) condensation of steam in the presence of heterogeneous centers (ODA impurity).

Ageev and Seleznev [3] suggested a different model of the effect of ODA on the mechanism of condensation of steam. It is assumed that initially a homogeneous condensation of steam occurs and nuclei are formed consisting of water molecules. These nuclei are centers of heterogeneous condensation of steam and ODA. The condensation of ODA results in the formation of monomolecular film on the droplet surface; this slows down further process of condensation and causes a rise of supercooling and a shift of the zone of intensive condensation downstream. However, the model of [3], while correctly predicting the shift of the zone of intensive spontaneous condensation downstream, fails to explain experimental facts such as the emergence of condensed phase long before the condensation jump and the increase in the average size of droplets that form in the process of condensation of steam in the presence of ODA.

Considered in this paper are three models of the effect of ODA on the mechanism of condensation under conditions of transonic flow of supercooled steam in a Laval nozzle. The first (two-zone) model is based on the assumption of the presence of two zones of spontaneous condensation (ODA and steam): at first a homogeneous condensation of ODA vapors is observed and a heterogeneous condensation of water vapors occurs on the resultant nuclei; this causes a decrease in the supercooling of flow and brings about a decrease in the intensity or even about degeneracy of homogeneous condensation of steam. The second model assumes binary nucleation in a two-component medium, i.e., the formation of nuclei containing molecules of water and ODA. The third model is a further development of the homogeneous–heterogeneous mechanism considered in [1, 2]. The physical processes are simulated in the same formulation as that in [4, 5], in view of generalization to the case of flow of two-component medium.

FORMULATION OF THE PROBLEM

A two-phase steam-droplet flow is considered, which is characterized by a high transonic velocity and finely dispersed moisture formed as a result of spontaneous condensation of supercooled steam. Because of the small size of droplets and high values of the flow velocity, the flow of two-phase medium is described by the equations of conservation of mass, momentum, and energy for the entire flow, disregarding the effects of viscosity and thermal conductivity,

$$\frac{\partial \rho}{\partial \tau} + \frac{\partial \rho W_i}{\partial x_i} = 0, \tag{1}$$

$$\frac{\partial \rho W_i}{\partial \tau} + \frac{\partial \rho W_i W_j}{\partial x_j} + \frac{\partial p}{\partial x_i} = 0, \tag{2}$$

$$\frac{\partial E}{\partial \tau} + \frac{\partial W_i (E + p)}{\partial x_i} = 0, \tag{3}$$

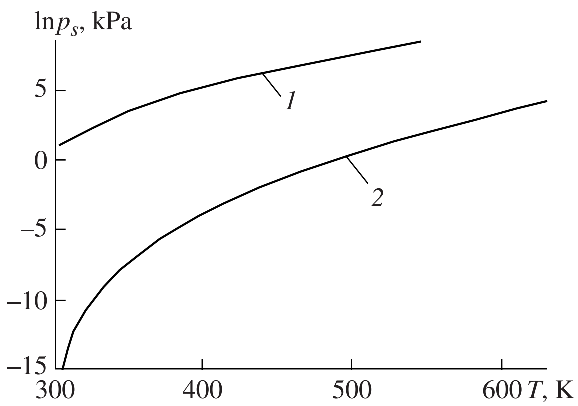

Fig. 1. The saturation pressure of vapors of (*1*) water and (*2*) ODA.

where ρ, W_i, and E denote the density, velocity, and total energy of the two-phase steam-droplet medium, respectively, and p is the pressure.

Three models were considered for describing the process of condensation of steam in the presence of ODA.

Two-Zone Model of Homogeneous Condensation

It is assumed that, in accordance with this model, two zones of spontaneous condensation of vapors of water and ODA as a result of nucleation may be observed. First, the ODA vapors condense because of a significantly lower saturation pressure as compared to steam (Fig. 1). The rates of nucleation of vapors of water and ODA are assumed to be independent and are calculated using the classical Volmer–Frenkel–Zel'dovich theory,

$$I_\chi = \frac{N_\chi^2}{\rho_{\chi l}}\left(\frac{2\sigma_\chi M_\chi}{\pi N_A}\right)^{1/2}\exp\left(-\frac{4\pi\sigma_\chi r_{\chi*}^2}{3k_B T}\right), \tag{4}$$

where N_χ is the number of molecules per unit volume of the gas phase, $\rho_{\chi l}$ is the density in the liquid phase, σ_χ is the surface tension coefficient, M_χ is the molecular mass, N_A is the Avogadro number, k_B is the Boltzmann constant, T is the steam temperature, and $\chi = 1$ for water and $\chi = 2$ for ODA.

The critical radius of nucleation in Eq. (4) is defined by the Kelvin formula,

$$r_{\chi*} = \frac{2\sigma_\chi}{\rho_{\chi l}R_\chi T\ln(p_\chi/p_{\chi s})}, \tag{5}$$

where R_χ is the gas constant, p_χ is the partial pressure, and $p_{\chi s}$ is the saturation pressure on a flat surface (at $r = \infty$), which corresponds to the steam temperature T.

It is further assumed that the heterogeneous condensation of ODA may be ignored in view of its very low concentration in the gas phase, and the heterogeneous condensation of steam may be observed on nuclei of both water and ODA. The rate of heterogeneous condensation of steam J depends on the droplet size (Knudsen number). So, the condensation or evaporation of very fine droplets at high values of the Knudsen number occurs in the free-molecule mode and is calculated in accordance with the Hertz–Knudsen kinetic model,

$$J = \kappa = \frac{4\pi r^2 p_\chi}{\sqrt{2\pi R_\chi T}}\left(1 - \sqrt{\frac{T}{\theta}}\right), \tag{6}$$

where J_κ is the rate of condensation in the free-molecule mode, r is the droplet radius, and θ is the temperature of droplets.

The rate of phase transitions for the case of relatively large droplets at low values of the Knudsen numbers is limited by the removal (during condensation) and input (during evaporation) of the heat of vaporization. In accordance with this, the rate of phase transitions is defined by the thermal resistance of the droplet surface and surrounding medium,

$$J = J_T = \frac{4\pi r\lambda(\theta - T)}{L}, \tag{7}$$

where λ is the coefficient of thermal conductivity in the gas phase and L is the latent heat of vaporization.

In order to determine the rate of condensation (evaporation) in the entire range of variation of the Knudsen number, an interpolation dependence is used that unites formulas (6) and (7),

$$J = \frac{J_\kappa J_T}{J_\kappa + J_T}. \tag{8}$$

The temperature of droplets in Eqs. (6) and (7) is found from the condition of equality of the saturated steam pressure at the curved surface of droplet to the pressure in the surrounding flow, whence follows

$$\theta = T_{1s} - \frac{(T_{1s} - T)r_{1*}}{r},$$

where T_{1s} is the steam saturation temperature on a flat surface (at $r = \infty$), which corresponds to partial steam pressure p_1.

The method of moments [2, 5] is used for the calculation of the evolution of droplets with respect to size as a result of phase transitions. Because two groups may be observed of droplets formed on the nuclei of water and ODA, respectively, two sets of equations for moments must be used, each set describing one of the groups of droplets.

Model of Binary Homogeneous Condensation

In accordance with this model, it is assumed that (for example, [6–9]), similarly to binary nucleation in the presence of acid vapors, binary spontaneous condensation may be observed in the two-component medium of vapors of water and ODA. In the case of

binary nucleation, the critical nucleus is characterized by two parameters, namely, the critical values of radius r_{χ^*} and X_* ($X_* = n_2/(n_1 + n_2)$, where n_1 and n_2 denote the number of molecules of water and ODA in the nucleus, respectively). According to the theory of binary condensation, these critical parameters are determined from the set of algebraic equations

$$\left.\begin{aligned} r_* &= \frac{2\sigma(X_*)}{\rho_{1l}R_1T\ln[p_1/p_{1s}(X_*)]}; \\ \ln[p_1/p_{1s}(X_*)] &= \frac{\rho_{2l}R_2}{\rho_{1l}R_1}\ln\left(\frac{p_2}{p_{2s}(X_*)}\right), \end{aligned}\right\} \quad (9)$$

where $\sigma(X_*)$ is the surface tension of a solution of composition X_*; $p_{1s}(X_*)$ and $p_{2s}(X_*)$ denote the equilibrium partial saturation pressures of vapors of water and acid over the flat surface of H_2O/ODA solution, in which the mole fraction of ODA is equal to X_*; the values of $p_{1s}(X_*)$ and $p_{2s}(X_*)$ are estimated using the Raoult and Henry laws.

The heterogeneous condensation of ODA may be ignored because of its low concentration in the gas phase, and the heterogeneous condensation of steam on nuclei of H_2O/ODA solution may be calculated using relations (6)–(8). The evolution of droplets with respect to size as a result of condensation is simulated by the method of moments.

Homogeneous–Heterogeneous Model of Condensation

This model is based on the assumption that only molecules of steam are involved in the homogeneous condensation, and the heterogeneous condensation may occur both on water nuclei being formed and on ODA molecules. Therefore, the presence of ODA is regarded as the presence of additional centers of heterogeneous condensation. The nucleation of steam is described by expressions (4) and (5), and the heterogeneous condensation on water nuclei and molecules of ODA is calculated using Eqs. (6)–(8). A combined approach is employed for simulation of the evolution of spectrum of droplets with respect to size as a result of condensation [5], which involves the use of the method of moments for moisture formed as a result of spontaneous condensation and of the method of δ-approximation for moisture condensing on ODA molecules.

CALCULATION RESULTS

The calculations were performed for conditions corresponding to experimental investigations in the case of flow of steam in a two-dimensional Laval nozzle with optically transparent side walls [1]. The steam at the nozzle inlet was slightly superheated or saturated. An aqueous emulsion of ODA was injected so that a uniform mixture of vapors of water and ODA was delivered to the nozzle inlet. The results of calculation and

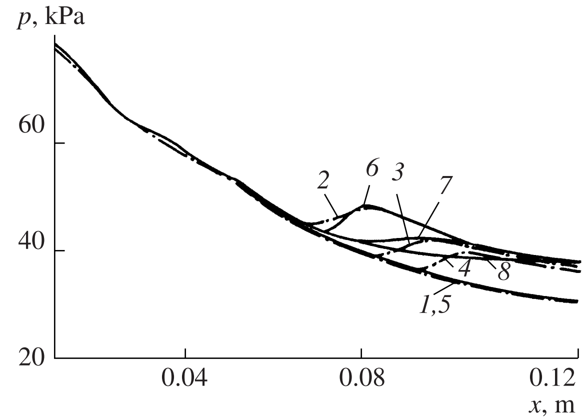

Fig. 2. The distribution of pressure along the nozzle: (*1–4*) experiments, (*5–8*) calculations; (*1, 5*) $T_0 = 433.15$ K, $C_0 = 0$; (*2, 6*) $T_0 = 378.15$ K, $C_0 = 0$; (*3, 7*) $T_0 = 378.65$ K, $C_0 = 8.2$ mg/l; (*4, 8*) $T_0 = 378.15$ K, $C_0 = 12$ mg/l.

measurement of pressure over the nozzle length along the axis are given in Fig. 2 (T_0 and C_0 denote the temperature of steam and concentration of ODA at the nozzle inlet, respectively, and x is the distance from the nozzle inlet). One can see that, given relatively high superheating of steam at the inlet, no condensation is present and a monotonic decrease in pressure is observed (curve *1*). When a pure slightly saturated steam is delivered to the nozzle, a jump of condensation arises due to nucleation (curve *2*). When ODA is injected, the condensation jump shifts downstream to the region of higher values of Mach number and is smoothed (curve *3*); this tendency increases with increasing concentration of ODA (curve *4*). The results of sounding the flow with a laser beam indicate that, when ODA is injected, the moisture appears much earlier, i.e., further upstream, as compared to the position of condensation jump under conditions of flow of pure steam. In the case of high concentration of ODA, the moisture appears even in the subsonic part of the nozzle. Measurements of light scattering reveal that the size of droplets increases with increasing concentration of ODA.

The flow under consideration was calculated using the solution of the set of Eqs. (1)–(3) in view of relations (4)–(9). First of all, note that no spontaneous condensation of ODA vapors occurred at the experimentally observed values of concentration $C_0 < 100$ mg/l, because the supersaturation p_2/p_{2s} was too low for nucleation to arise. Therefore, the mechanism of the effect of ODA in accordance with the two-zone model of homogeneous nucleation was not realized under our experimental conditions, although it may possibly be observed at higher concentrations of ODA; nor does the model of binary homogeneous condensation provide an adequate description of the experimentally observed effect of ODA on the characteristics of flow. According to expression (9), the basic effect taken into account by

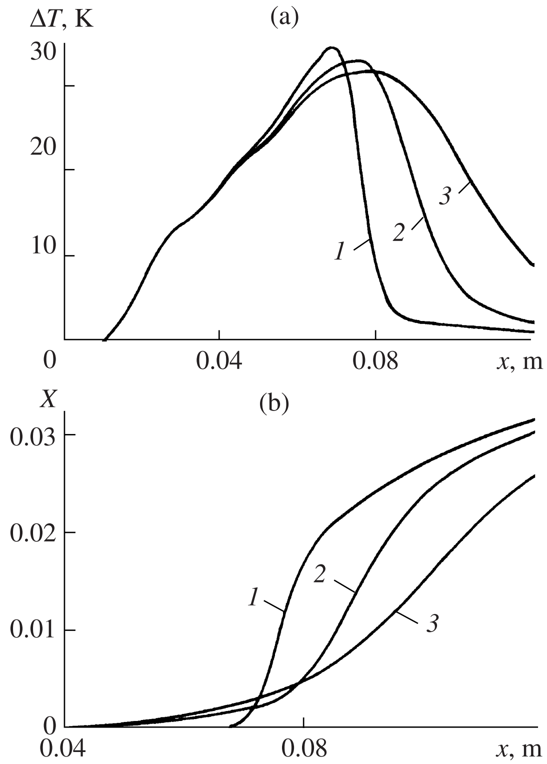

Fig. 3. The effect of ODA concentration on the distribution of (a) steam supercooling and (b) humidity along the nozzle: (*1*) T_0 = 378.15 K, C_0 = 0; (*2*) T_0 = 378.65 K, C_0 = 8.2 mg/l; (*3*) T_0 = 378.15 K, C_0 = 12 mg/l.

this model consists in reduction of surface tension owing to the presence of ODA; this in turn causes a decrease in the critical radius of condensation r_* and, consequently, in the value of supersaturation p_2/p_{2s} at which the process of nucleation may begin. Therefore, the model of binary condensation predicts the displacement of the zone of intensive condensation upstream, which contradicts the experimental data.

The calculation results demonstrate that, of all of the considered models, it is only the homogeneous–heterogeneous condensation model, which takes into account the heterogeneous condensation on water nuclei and on molecules of ODA, that is capable of reproducing all of the experimentally observed effects caused by the addition of ODA. This model is capable of predicting both the faster emergence of finely divided moisture and the displacement of the zone of intensive condensation downstream. In performing the calculations, it is assumed that heterogeneous condensation occurs only on some part of ODA molecules. For this purpose, a coefficient is introduced taking into account the fraction of active molecules which are centers of heterogeneous condensation of steam. In all calculations, this coefficient is taken to be 0.01.

Figure 3 gives the calculated effect of ODA on the distribution of steam supercooling and humidity. Here, the supercooling ΔT is determined as the difference

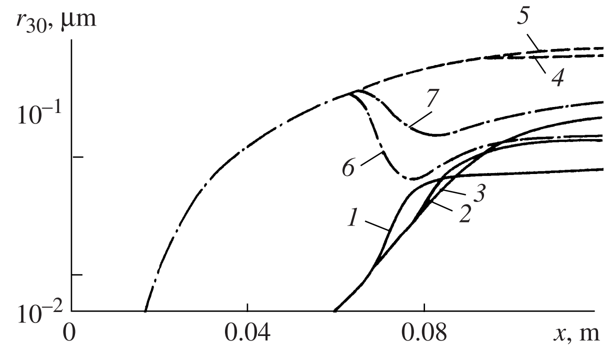

Fig. 4. The variation of volume average radii of droplets along the nozzle: (*1–3*) H_2O droplets, (*4*, *5*) ODA droplets, (*6*, *7*) H_2O + ODA droplets; (*1*) T_0 = 378.15 K, C_0 = 0; (*2, 4, 6*) T_0 = 378.65 K, C_0 = 8.2 mg/l; (*3, 5, 7*) T_0 = 378.15 K, C_0 = 12 mg/l.

between the temperatures of saturation and steam, and the humidity X as the ratio of mass of the liquid phase per unit volume to density of steam-droplet medium. It follows from Fig. 3 that the presence of ODA causes the smoothing of the condensation jump and, at high concentrations, may even result in its complete disappearance. This effect is caused by the decrease in supercooling of steam as a result of its condensation on ODA molecules delivered to the nozzle.

Figure 4 gives the variation of volume average radii of droplets r_{30} along the nozzle axis. Curves *1–3* are reflective of the evolution of the radii of droplets formed as a result of spontaneous condensation of steam (H_2O droplets), curves *4* and *5* relate to the droplets formed on ODA molecules (ODA droplets), and curves *6* and *7* relate to average radii of the entire system of droplets including droplets of both types (H_2O + ODA droplets). It is obvious that a monotonic growth of both H_2O droplets and ODA droplets is observed as a result of heterogeneous condensation. In the presence of ODA, the growth of H_2O droplets is slower at first; however, in the exit section of the nozzle, the size of these droplets increases with concentration of ODA. When the concentration of ODA increases, a slight increase is observed in the size of ODA droplets in the exit section of the nozzle. The nonmonotonic pattern of variation of average size of the system of H_2O + ODA droplets is explained by the much larger size of ODA droplets and their significantly smaller number (number density) compared to H_2O droplets. Therefore, the average size of the system of H_2O + ODA droplets in the inlet (subsonic) section of the nozzle corresponds to the radius of ODA droplets; after the emergence of nuclei as a result of nucleation of steam, this size approaches the radius of H_2O droplets. The increase in the average size of droplets in the vicinity of the nozzle exit with increasing concentration of ODA agrees with the experimental data of [1].

An important feature of flow of spontaneously condensing steam is the possibility of emergence of

unsteady self-oscillatory modes. This phenomenon is due to the latent heat of vaporization during condensation, to the formation of unsteady waves and their interaction with the zone of condensation. The emergence of self-oscillation may be dangerous from the standpoint of fatigue failure of exit edges of nozzle arrays when the values of natural and induced frequencies coincide. The calculation results confirmed that the introduction of ODA causes the stabilization of unsteady flow and transition from self-oscillatory to steady quasi-equilibrium flow.

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